

Correlation of the Material Properties of Calcium Carbonate Filled Polypropylene with the Filler Surface Energies

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ABSTRACT: The physical and mechanical properties of polypropylene (PP) were measured and compared with those of PP composites filled with calcium carbonate modified with sodium polyacrylate, stearic acid, or both. The variations in the mechanical properties showed a high degree of correlation with the surface energies of the fillers, as determined by inverse gas chromatography. The results con-

firmed the usefulness of inverse gas chromatography for characterizing the compatibility of polymer–filler combinations. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1951–1955, 2003

Key words: chromatography; surfaces; fillers; poly(propylene) (PP)

INTRODUCTION

The majority of common household and automotive applications of thermoplastics involves their use in conjunction with mineral fillers. The ability to tailor-design composites by surface modification has changed the emphasis from the mineral being considered a simple filler, giving cost reduction but little else, to it providing additional benefits in terms of processing and end properties.^{1,2} Particulate composites can have improved mechanical properties and stability with respect to the polymer alone. The benefits obtained depend critically on the surface properties of each component being appropriate so that good bonding and compatibility between them is ensured and so that the filler material can be well dispersed in the polymer matrix. In particular, this requires the surface energetics of the mineral and polymer to be carefully matched.

A number of methods can be used for measuring the surface properties of polymers,^{3–5} although inverse gas chromatography (IGC) has recently been shown to be a robust and reliable method for the study of surface characteristics of a wide range of minerals and polymers.^{6,7}

A commonly used filler mineral, particularly in polyolefins, is calcium carbonate (CaCO₃); its addition confers improved toughness and rigidity to composites. However, it usually needs to be modified before it

can be successfully incorporated into polymers. A treatment with stearic acid or another acid is often used to assist with the wetting and dispersion of the filler. Ahsan and Taylor⁸ measured the impact strength of polypropylene (PP)–CaCO₃ composites in which the filler had been treated with various levels of stearic acid (SA). They found that the surface free energy measured by IGC fell with the SA treatment up to monolayer coverage and that there was a corresponding increase in the impact strength. Some years ago, Schreiber et al.⁹ used IGC to investigate the plasma modification of CaCO₃ in polyethylene and poly(vinyl chloride).

The IGC characterization of pure CaCO₃ and the effect of a treatment with a dispersing agent [sodium polyacrylate (PAC)] and SA was recently completed.¹⁰ In this article, we describe a range of mechanical properties of PP composites prepared with these CaCO₃ materials and demonstrate their correlation with the polymer and filler surface energies measured by IGC.

EXPERIMENTAL

Materials

The PP used was a commercially available grade (GWE 27 PP) from ICI (Wilton, UK). It had a melt-flow index of 4.2 at 230°C, a density of 905 kg m⁻³, a melting range of 165–175°C, a tensile yield stress of 34.5 MPa, and a flexural modulus of 1.50 GPa. To avoid the compositional uncertainties involved in CaCO₃ obtained from natural sources, pure samples of calcite with a Brunnauer-Emmett-Teller (BET) surface area of 2.68 ± 0.05 m² g⁻¹ were prepared in the

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TABLE I
Mechanical and Physical Property-Results of Filled PP Moldings

		PP	PP + PCC	PP + PCC-SA	PP + PCC-PAC-SA
Color	<i>L</i>		87 (3)	85 (2)	84 (3)
	<i>a</i>		0.5 (0.01)	-0.5 (0.02)	-0.5 (0.03)
	<i>b</i>		3.0 (0.2)	2.5 (0.1)	2.3 (0.1)
Gloss	20°	81 (1)	40 (3)	59 (2)	54 (4)
	60°	106 (4)	58 (3)	74 (2)	71 (2)
	85°	101 (1)	86 (2)	97 (1)	95 (2)
Falling-weight impact strength	Peak force (N mm ⁻¹)	167 (37)	500 (15)	1220 (60)	970 (40)
	Peak energy (J mm ⁻¹)	1.7 (0.2)	3.5 (1.2)	8.3 (1.3)	5.2 (2.1)
	Fail energy (J mm ⁻¹)	1.3 (0.2)	3.7 (1.1)	9.1 (1.5)	4.6 (1.3)
Izod strength	Notched (kJ m ⁻²)	1.4 (0.2)	2.6 (0.2)	4.6 (0.1)	3.4 (0.4)
	Unnotched (kJ m ⁻²)	60 (1)	30 (3)	45 (3)	32 (2)
Flexural properties	Modulus (MPa)	1480 (110)	2840 (125)	2710 (102)	2920 (117)
	Yield strength (MPa)	32 (1)	38 (2)	44 (1)	46 (1)

The standard deviations of measurements are in parentheses.

laboratory. The preparation and properties were described previously, along with the conditions under which the surface modification was carried out.¹⁰ In summary, three samples of CaCO₃ were used: pure precipitated calcite (PCC), PCC coated with a monolayer of SA (PCC-SA), and PCC treated with PAc and then SA (PCC-PAC-SA). Scanning electron microscopy analysis showed the average particle size to be approximately 1 μm.

Polymer property characterization

The fillers were compounded into PP at a loading of 40 wt % on an APV MP2030 twin-screw extruder (Peterborough, UK) at a constant 50% torque. The die temperature was 210°C with a screw speed of 250 rpm. After drying overnight at 60°C in a Conair Churchill (Wokingham, UK) desiccant dryer, each compound was injection-molded in an Arburg 320M Allrounder injection molder with a mold temperature of 60°C and a die temperature of 230°C, yielding 80 mm × 80 mm × 2 mm plaques or 80 mm × 10 mm × 4 mm bars. Test specimens, also produced for the unfilled PP, were conditioned for 4 days at 23°C and 50% relative humidity before the testing.

The plaque color was measured with a Minolta chrometer, which gave *L* (whiteness), *a* (blue/green), and *b* (red/yellow) values; the plaque gloss was measured at 20, 60, and 85° with a Gardner BYK haze-gloss meter. The falling-weight impact strength of the plaques was measured with a Rosand IFIW5 impact tester (Sturbridge, UK). The notched and unnotched Izod strengths of the bars were measured with a Ceast pendulum tester (Pianezza, Italy). The flexural modulus was measured with a Monsanto T10 tensometer by the three-point bending technique.

Chromatography

For the preparation of IGC column packings, the homopolymer and composites were pelleted and ground in a Janeke and Kunkel mill under liquid nitrogen. The material was sieved to produce 425–850-μm fractions and packed into a gas chromatography column in the usual manner⁶ for analysis. The chromatography system was based on a PerkinElmer Autosystem XL gas chromatograph (Beaconsfield, UK) and was described in detail previously.¹⁰

After being loaded into the chromatograph, the columns were preconditioned at 120°C for 24 h under a flow of the nitrogen carrier. A series of 0.1-μL aliquots of the probe vapors were injected with a Hamilton syringe (Aldrich, UK) over a range of temperatures. Each retention time was the result of at least three elutions agreeing within experimental uncertainty. The usual checks⁷ were made to confirm that the measurements were being made under infinite dilution conditions.

RESULTS AND DISCUSSION

Physical testing of PP injection moldings

The characterization of each of the filled polymers is given in Table I. The PP-CaCO₃ composites had a lower surface gloss than the parent homopolymer at all three measuring angles because of the particles at the surface scattering light and reducing the reflected light measured. This effect was directly correlated to the particle size if the filler was well dispersed, with larger, coarser particles giving greater scattering and, therefore, lower gloss. Poorly dispersed particles formed large, coarse aggregates and also reduced the gloss. This accounts for the fact that the gloss was

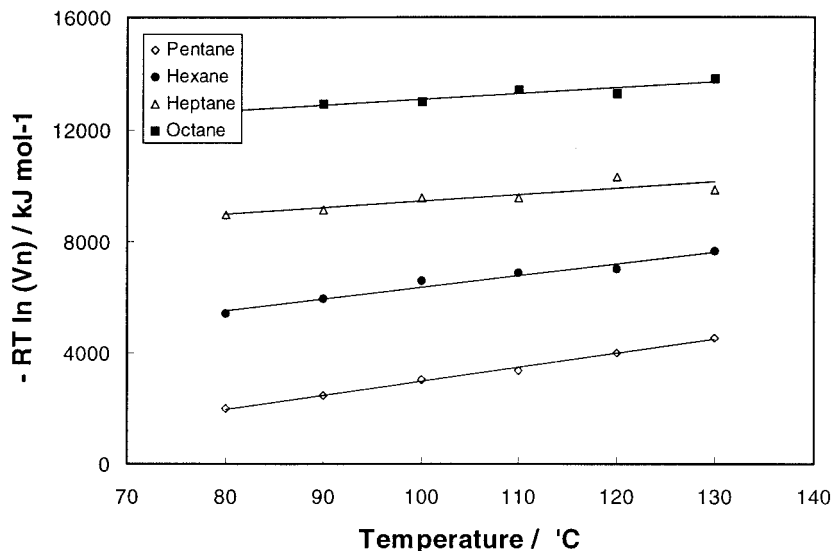


Figure 1 Retention diagrams for alkane probes on PP.

reduced most when unmodified CaCO_3 was used. No significant differences were seen between plaques for which PAC, added to aid dispersion, was used, and this confirmed that both PP-SA and PP-PAC-SA were well dispersed in the PP matrix. Similarly, a treatment with PAC made no significant difference in the color results with respect to SA.

The mechanical properties of the polymer were significantly altered with the addition of the filler. The falling-weight impact strength, the Izod impact strength, and the flexural modulus all markedly increased. The PP homopolymer was brittle and had a relatively low impact strength. The CaCO_3 addition modified this by a crack-pinning effect in which the filler particles retarded microcrack propagation.¹ The addition of the filler to PP doubled the impact fail energy, although the surface modification of the filler greatly enhanced the increase. The Izod impact strength results followed the same trend, with the moldings containing the surface-modified PCCs having considerably higher impact strengths. It is perhaps surprising that the addition of PAC before SA reduced the beneficial effect of the latter. The flexural modulus increased with the filler addition because of the greater rigidity of the filler with respect to the polymer matrix. Taken together, these results demonstrate that there was good dispersion of the PCC-SA material through the PP matrix and also that there was good adhesion between the polymer and the filler.

Gas chromatography measurements

For good impact properties, the differences between the polymer matrix and mineral surface should be minimal.^{11,12} IGC allows the convenient measurement of surface energies. Because PP is a polyolefin, it

would be expected to show only dispersive, nonpolar contributions to the surface energy and to give negligible polar contributions. The IGC retention diagrams for alkane probes on PP between 80 and 130°C are shown in Figure 1. As expected from adsorption onto the surface below the glass transition of the polymer, the relationship is linear. The retention volume (V_n) is the volume of the carrier gas required to elute the probe under standard conditions⁶ and is related to the standard free energy of adsorption (ΔG_a°):

$$\Delta G_a^\circ = \Delta H_a^\circ - T\Delta S_a^\circ = -RT \ln V_n + k \quad (1)$$

where k is a constant related to the choice of standard states.⁹ The plot yields the isosteric enthalpy of adsorption (ΔH_a°). The data give values of 30–43 kJ mol⁻¹ for pentane to octane, respectively. These are close to the enthalpies of vaporization of the probes and indicate that there was, as expected, little specific interaction between the alkane probes and the PP surface.

A consideration of the surface free energy of the polymer is more instructive. The free energy change for the adsorption of a single methylene group ($\Delta G_a^{\circ, \text{CH}_2}$) can be determined from the difference in the free energies of adsorption for successive alkanes in a homologous series:

$$\Delta G_a^{\circ, \text{CH}_2} = -RT \ln \left(\frac{V_n(n+1)}{V_n(n)} \right) \quad (2)$$

where n is the number of carbons in the alkane. $\Delta G_a^{\circ, \text{CH}_2}$ is found at a constant temperature from a linear plot for a series of alkane probes of $RT \ln(V_n)$ versus the number of carbon atoms. The dispersive

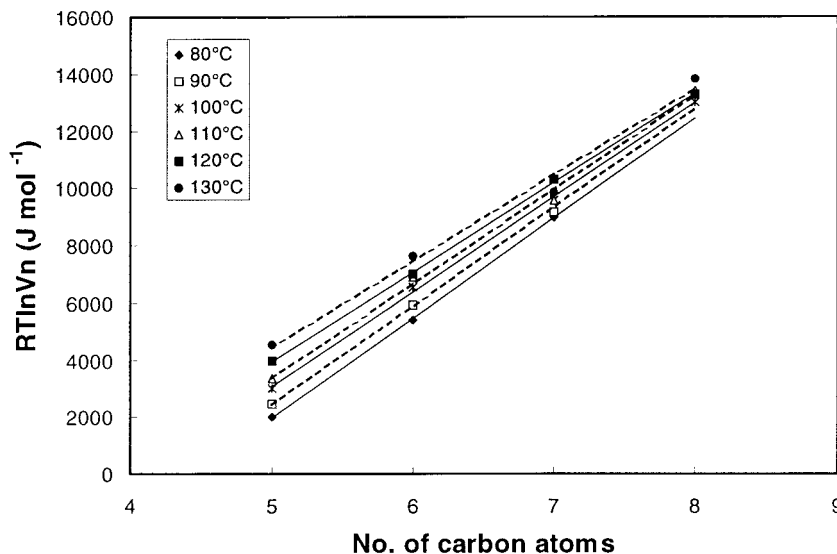


Figure 2 Plot of $RT \ln V_n$ versus the number of carbon atoms for alkane probes on PP.

component of the surface free energy (γ_s^d) can then be calculated as follows:^{13,14}

$$\gamma_s^d = \frac{1(-\Delta G_a^{o,CH_2})^2}{\gamma_{CH_2}(2Na_{CH_2})} \quad (3)$$

where N is Avogadro's number; γ_{CH_2} is the surface tension of a hypothetical surface containing only methylene groups, and a_{CH_2} is the cross-sectional area of a methylene group ($\approx 0.06 \text{ nm}^2$). The plot mapped according to eq. (2) is shown in Figure 2 and, in conjunction with eq. (3), yields values of γ_s^d of $36 \pm 2 \text{ mJ m}^{-2}$ between 110 and 80°C. These agree well with literature values measured by other techniques quoted between 30 and 35 mJ m^{-2} .¹⁵

The aim of this work was to correlate the physical property results with the surface energies of the polymer and fillers. The former are summarized briefly with reference to the unfilled PP in Table II. Also shown in the table are the IGC-measured surface free energies of the fillers.¹⁰ It is apparent that the PCC and PCC treated only with PAc had significantly higher surface energies than the polymer, whereas those

treated solely with SA had a somewhat lower surface energy. Our previous work¹⁰ showed that the PAc-treated surfaces retained appreciable polarity and that the dispersant prevented interactions with some parts of the surfaces. Complete coverage with SA produced a surface that was effectively alkane-like in its interactions. It is clear from Table II that the incorporation of this filler into PP gave the best enhancement of its physical properties.

In a polymer matrix, good wetting of the filler surface is necessary for thorough dispersion. Any agglomerated filler will act as a defect that can initiate impact failure. However, the adhesion between the filler and matrix should not be too strong because this will prevent debonding at the interface, which is necessary for dissipating the energy in an impact and, therefore, imparting toughness to the composite.¹⁶ Pukanszky¹⁷ studied interfacial interactions in PP composites and correlated their yield stresses with their interaction strengths (as measured by the contact angle). SA-treated CaCO_3 gave a lower yield stress and lower interaction than untreated CaCO_3 in PP. The IGC method has an advantage, in that it can be ap-

TABLE II
Summary of Physical Testing Results of PP Moldings with 40 wt % Filler

System	Relative properties of moldings (PP = 1)					Surface free energy (mJ m^{-2}) ^a
	Notched Izod strength	Impact strength (fail energy)	Impact strength (peak force)	Yield strength	Modulus	
PP	1	1	1	1	1	36 ± 2^b
PP + PCC	1.9	2.8	3.0	1.2	1.9	39–48
PP + PCC–SA	3.3	7.0	7.3	1.4	1.8	24–31
PP + PCC–PAc–SA	2.4	3.5	5.8	1.4	2.0	35–43

^a Values measured at 80–110°C.

^b Surface energy of PP homopolymer.

plied to finely divided particulates such as fillers, the surface energies of which are difficult to measure by contact angles.

CONCLUSIONS

We have demonstrated a good correlation between the physical properties of PP-CaCO₃ composites with the surface energies of the filler, as measured by IGC. The optimum mechanical properties of those studied were obtained when the filler was completely coated to mask any polar interactions so that the surface free energy of the filler was comparable with (slightly lower than) that of the polymer matrix.

Our results further demonstrate the utility of IGC for measuring the surface properties of composite materials and show how such results may be used to engineer the surfaces of fillers to give desired properties to a composite system.

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